Role of Disorder in Mn:GaAs, Cr:GaAs, and Cr:GaN

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Abstract

We present calculations of magnetic exchange interactions and critical temperature T_c in $Ga_{1-x}Mn_xAs$, $Ga_{1-x}Cr_xAs$ and $Ga_{1-x}Cr_xN$. The local spin density approximation is combined with a linear-response technique to map the magnetic energy onto a Heisenberg hamiltonion, but no significant further approximations are made. Special quasi-random structures in large unit cells are used to accurately model the disorder. T_c is computed using both a spin-dynamics approach and the cluster variation method developed for the classical Heisenberg model.

We show the following: (*i*) configurational disorder results in large dispersions in the pairwise exchange interactions; (*ii*) the disorder strongly reduces T_c; (*iii*) clustering in the magnetic atoms, whose tendency is predicted from total-energy considerations, further reduces T_c. Additionally the exchange interactions $J(R)$ are found to decay exponentially with distance R^3 on average; and the mean-field approximation is found to be a very poor predictor of T_c, particularly when $J(R)$ decays rapidly. Finally the effect of spin-orbit coupling on T_c is considered. With all these factors taken into account, T_c is reasonably predicted by the local spin-density approximation in MnGaAs without the need to invoke compensation by donor impurities.

Dilute magnetic semiconductors (DMS), i.e. semiconductors doped with low concentrations of magnetic impurities (usually Cr, Mn, or Co), have attracted much interest because of their potential application to spintronics[1, 2] . $Ga_{1-x}Mn_xAs$ is the most widely studied DMS, and it continues to attract interest because it is one of the few DMS where it is generally agreed that the magnetism is carrier-mediated. (This is important in spintronics because the magnetic state can be manipulated by electrical or optical means.)

In recent years Curie temperatures in $Ga_{1-x}Mn_xAs$ have risen steadily, reaching $\sim$170K for $x\sim$0.08 when grown in thin films annealed at low temperature [3, 4, 5]. It is generally believed defects (probably Mn interstitials) migrate out of the as-deposited films during the anneal, largely eliminating donor defects that hamper ferromagnetism. Since most practical applications of spintronics require room-temperature operation, a crucial question is then, what is the ultimate limit to T_c in the DMS compounds, and in $Ga_{1-x}Mn_xAs$ in particular?

This question was first addressed by Dietl in his now classic paper[6], where he predicted a wide range of T_c in tetrahedrally coordinated alloys. This stimulated a great deal of interest, although there is a growing consensus that most of the claims of that paper were artifacts of the assumptions in his original model. On the other hand, Akai[7] first used the local spin-density approximation (LSDA) to estimate T_c within the Coherent Potential Approximation (CPA) in (In,Mn)As; he argued that a double exchange mechanism was a more appropriate description of the magnetism than the *pd* exchange assumed by Dietl. Since then LSDA calculations of exchange interactions have been performed by a variety of groups [8, 9, 10, 11, 12, 13], usually extracting exchange parameters by calculating total energies of a fixed atomic but multiple-spin configurations, or by a linear-response technique within the CPA.

To date, disorder has almost always been neglected or treated within some mean-field (MF) approximation (MFA), either in the computation of the exchange parameters themselves, or in the subsequent analysis of magnetization $M(T)$ at finite-temperature, or both (though better treatments within $k \cdot p$ theory has been reported [14]). The LSDA+MF predict a rather high T_c for $Ga_{1-x}Mn_xAs$ (typically 350$\sim$400 K for $x\sim$0.08 [13]). The large discrepancy with experiment (at least in Mn:GaAs) is usually attributed to the very large numbers of compensating defects in real samples, which reduce T_c [3, 4, 5]. The situation remains somewhat uncertain because the number of defects still remaining in the best samples to date is not known.

This Letter addresses the issue of the ultimate limit to T_c in some DMS alloys (focusing on Mn:GaAs) by adopting relatively rigorous approach to the calculation of the magnetic exchange interactions and T_c. Random alloys are approximated by large (128-250 atom) supercells where special quasirandom structures (SQS) [15] are used for the cation sublattice. Using a linear-response technique within the LSDA and the linear-muffin-tin orbitals method[16, 17], the magnetic energy is mapped onto a Heisenberg form[18]

$$H = -\sum_{ij} J(R_{ij})\, \hat{e}_i \cdot \hat{e}_j \tag{1}$$

where the sum is over all pairs ij of magnetic atoms. To model $M(T)$ and T_c, Eq.(1) is treated classically and integrated using a spin-dynamics (SD) technique[19]; alternatively $M(T)$ is estimated by the cluster variation method (CVM)[20] adapted[21] to solve Eq.(1). Thus it is evaluated without recourse to empirical parameters or to the MFA. We show that the widely used MFA turns out be a very poor predictor of $M(T)$ in these disorded, dilute alloys, dramatically overestimating T_c.

With SQS we can rather precisely mimic a fully random configuration, but it is also possible to consider configurations that deviate from random. This can be important because LSDA predicts a strong attractive interaction between magnetic elements [8], which implies a tendency towards clustering. In brief, we show that

- the disorder induces large fluctuations in $J_{ij} \equiv J(R_{ij})$ for every connecting vector R_{ij};
- The fluctuations in J_{ij} *reduce* T_c relative to the configurationally averaged $\overline{J}_{ij} = \langle J_{ij} \rangle$;
- clustering *reduces* T_c, while ordering of the magnetic elements *increases* T_c.

Fig. 1 shows J_{ij} computed for an ensemble of 108-cation (216-atom) random supercells following the method of Ref.[17], for $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Cr_xN$ alloys at x=4.6% and x=8.3%. $3\times3\times3$ k-points were used, enabling the calculation of J to very distant neighbors. We chose these two alloys because they are approximately representative of limiting cases. For Cr:GaN, the GaN host has a wide bandgap, and the Cr t_2 level falls near midgap. It broadens into an impurity band with 1/3 occupancy, and is believed to be responsible for the ferromagnetic exchange. For Mn:GaAs, most of the weight of the Mn t_2-derived state falls below the valence band maximum. A second t_2 impurity band about 0.1 eV above the valence band maximum is mainly responsible for the ferromagnetic exchange coupling

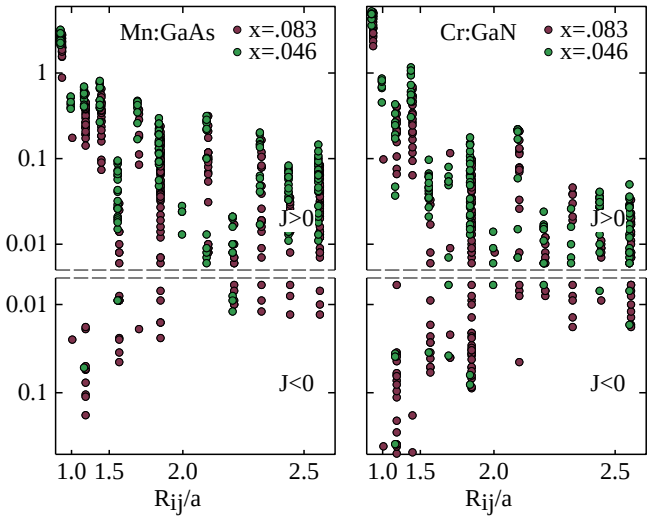

FIG. 1: Pair exchange interactions $J(R_{ij})$, in mRy, for Mn:GaAs and Cr:GaN at two different concentrations as a function of R_{ij}^3. R_{ij} is measured in units of the lattice constant a.

in this case; the strength of $J(R)$ depends critically on the amount of Mn character in this band[22]. Katayama-Yoshida used the x-dependence of $J_0 = \sum_R \overline{J}(R)$ (computed within the CPA) to identify the ferromagnetism obtained from LSDA with model theories[13]. Within the CPA, $J_0 \sim x^{1/2}$ for Cr:GaN, which corresponds to a double-exchange model, while Mn:GaAs displays character intermediate between $J_0 \sim x^{1/2}$ and the pd exchange ($J_0 \sim x$) usually assumed by $k \cdot p$ models [6, 23].

Comparing Cr:GaN to Mn:GaAs, Cr:GaN shows substantially stronger nearest-neighbor (NN) interactions, owing to its small lattice constant; however $\overline{J}(R_{ij})$ decays much more rapidly with R_{ij}. This is because the wave function overlap between transition metal d states decays much more rapidly for midgap states than near band-edge states. Evident also is the large dispersion in J_{ij} for fixed R_{ij} (note J is drawn on a log scale): the root-mean square fluctuations $\Delta J_{ij} = \sqrt{\left\langle J_{ij}^2 - \bar{J}_{ij}^2 \right\rangle}$ are roughly comparable to $\overline{J}$. However ΔJ_{ij} *increases* with x, and is substantially larger for the wide-gap case (Cr:GaN). Note that there is little evidence in either Cr:GaN or Mn:GaAs for oscillatory RKKY-like behavior, which in the simplest approximation predicts $J(R) \sim \cos(2k_F R)/R^3$. Instead, $\overline{J}(R)$ decays roughly exponentially in R^3, corresponding to a Fermi surface with imaginary wave number, as would obtain if the coupling were described by tunneling via a disordered impurity band[24].

We now apply Eq.(1) to compute $M(T)$, focusing on T_c. Mean-field theory, which estimates the effective field at each site from the average field contributed by other sites,

predicts T_c well above room temperature both in Mn:GaAs and Cr:GaN[13, 25]. In spite of the rather strong differences in the form of $J(R)$ (Fig. 1), mean-field theory predicts that Mn:GaAs and Cr:GaN have roughly similar T_c for $x{\sim}0.08$[25]. This is because the NN interaction in the latter case is strongest, but the J decays faster with R, leading to a comparable mean-field[26] estimate $\overline{T}_c^{MFA}$.

But it should be evident from Fig. 1 that the MFA is of questionable reliability. First, it is well known that for dilute alloys there is a percolation threshold for the onset of ferromagnetism. (The threshold in the present case cannot be readily mapped to known models because $J(R)$ is nonneglible for a rather large number of neighbors.) Moreover, the large fluctuations $\Delta J(R)$ may strongly affect T_c, especially since $\Delta J(R)$ itself is purely a function of the environment[8], and consequently of the local percolation path.

To obtain a precise estimate for $M(T)$ and T_c, we adopt a spin-dynamics approach[19]. A 200 atom SQS structure (250 atom for the 4% alloy) was used to mimic the random alloy. From the TM atoms in the SQS structure, a supercell containing $\sim$ 2000 Mn or Cr atoms was constructed to make a simulation cell for prosecuting spin-dynamical simulations. Following the method described in Ref.[19], the Landau-Lifshitz (L-L) equation was integrated numerically at a fixed temperature allowing the system to equilibrate, followed by a simulation for $\sim 2 \times 10^6$ atomic units. The L-L equations were integrated with the Bulirsch-Stoer method. As the L-L equation is a first-order equation, global deamons were used for the heat bath[19], to ensure ergodic behavior. The average magnetization $\overline{M}(T)$ was computed as a function of temperature, and T_c was estimated from the inflection point in $\overline{M}(T)$. Owing to finite-size effects and the stochastic character of the simulation, T_c could be determined to a precision of $\sim$5%.

Also we employed a CVM approach recently adapted to the classical Heisenberg hamiltonion[21]. This relatively simple scheme has been found to be accurate in simple $3d$ magnets, overestimating T_c by $\sim$5% (similar to the usual CVM for the Ising hamiltonion[27]). We can check the validity both methods in the DMS case by comparing their predictions of T_c. Fig 2 shows T_c determined by both methods for $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Cr_xAs$: agreement between the two methods is $\sim$10%, which is quite satisfactory considering the complexity of the J_{ij}. $\overline{T}_c^{MFA}$ is also shown: evidently the MFA rather badly overestimates T_c. $\overline{T}_c^{MFA} > T_c$ by $\sim$200K in the Mn:GaAs alloy, and by a somewhat larger amount in Cr:GaAs. The discrepancy is still more dramatic in Cr:GaN (not shown); we find $T_c < 50$K

for all concentrations studied while $\overline{T}_c^{MFA} \sim 600$K[25]. Indeed we have found this generally to be the case when $J(R)$ decays rapidly or when $\Delta J(R)/J(R)$ is not small.

These results stand in stark contrast to the $\sim$15% discrepancy between T_c^{MFA} and T_c typically found in simple metals. The reason is easily understood by considering the effective field a mean-field atom sees, $\vec{H}_i^{eff} = \sum_j J_{ij}\hat{e}_j$. From the exponential decay of $J(R)$, it is evident that H_i will be dominated by the nearest neighbors. But for dilute alloys, near-neighbors are not sufficent to form a percolation path. This is immediately evident in the extreme case of a NN pair of magnetic atoms well separated from any other magnetic atoms: the contribution to T_c^{MFA} from this pair would be high, even though the pair would actually contribute nothing to ferromagnetism.

In Ref. [10] a small discrepancy between T_c^{MFA} and a more sophisticated calculation for T_c was reported. In that calculation the CPA was used to construct an average $\overline{J}_{ij}$ and $M(T)$ modeled by constructing a fcc lattice of magnetic atoms, using concentrated-weighted $\overline{J}_{ij}$ for the exchange parameters. It would seem that their conclusions are an artifact of the neglect of configurational disorder (except in the computation of $\overline{J}_{ij}$). Better would be to estimate $\overline{J}_{ij}$ within the CPA, and then construct a *disordered* simulation cell using the $\overline{J}_{ij}$ to estimate $M(T)$. Still this approach neglects fluctuations ΔJ, which as we have seen are comparable to $\overline{J}_{ij}$ itself. To assess the effect of fluctuations, we repeated the calculation for T_c within the CVM, replacing the environment-specific J_{ij} with the configurationally averaged $\overline{J}_{ij}$. For $Ga_{1-x}Mn_xAs$ at x=0.08, the effect of disorder ($\overline{J}_{ij} \to J_{ij}$) was to reduce T_c by 50 K. (It is interesting that the MFA predicts the *opposite* trend, because of an artificial tendency for $M^{MFA}(T)$ to track whichever site i has the largest $\vec{H}_i^{eff}$. Then $T_c^{MFA} - \overline{T}_c^{MFA}$ is positive[26] and increases with $\Delta J/J$. This explains why a tight-binding+MF analysis[24] predicted that disorder *increases* T_c.)

We next consider the effects of nonrandomness. As noted above, real DMS alloys should exhibit some clustering owing to the attractive interaction between magnetic elements[8]. The true situation is complicated by the nonequilibrium growth required to stabilize the alloy in the zincblende structure. Nevertheless the Mn-Mn or Cr-Cr binding energy is calculated[8] to be an order of magnitude larger than the growth temperature ($\sim$250K), and some pairing or other clustering should be expected, particularly since films must be annealed to obtain good T_c. There is some experimental evidence for a tendency to cluster[28].

The effect of clustering on T_c in $Ga_{0.92}Mn_{0.08}As$ was studied by a simple model. To

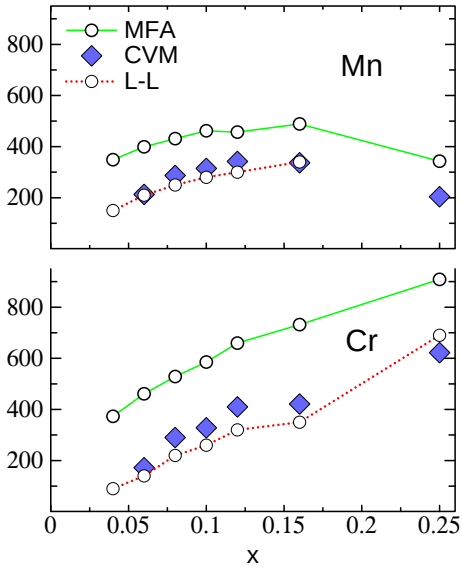

FIG. 2: Dependence of T_c (K) on x in $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Cr_xAs$. Solid lines: T_c computed from the MF $\overline{T}_c^{MFA}$[26]. Dotted line: T_c extracted from spin-dynamics simulations of Eq. 1. Diamonds: T_c computed from the Heisenberg Cluster Variation Method.

characterize the configurational disorder we adopt the standard Ising formalism, and assign $\sigma = \pm 1$ to each cation site (+1 for Mn and −1 for Ga). The random (SQS) configuration was constructed by searching for configurations which best approximate the ideal random configuration for pair correlation functions $P_{R_{ij}} = \langle \sigma_i \sigma_j \rangle$ (and some higher-order correlation functions) up to some fixed distance. For a random configuration, $P_R = (2x-1)^2$ independent of R. To parameterize the clustering in a simple manner, we adopted the NN pair correlation function P_1 as a measure of clustering. Starting from an initial SQS configuration, a simulated annealing cycle was performed by generating a set of site configurations with increasing P_1, corresponding to longer annealing times (For simplicity, $P_n (n > 1)$ was optimized to be $(2x-1)^2$ for each configuration.) J_{ij} and T_c were computed by the CVM and MFA[26] as a function of P_1; see Fig. 3. T_c is rather strongly *reduced* with increasing P_1. This is perhaps not surprising since increased clustering implies more distant average separation between atoms, which is deleterious to links in the percolation path. Even within the MFA T_c changes slightly, albeit for a different reason. In that case, there is an increase in NN pairs, which would increase T_c, but at the same time there is some increase in the likelihood of *three-* and higher body neighbors. The presence of a third neighbor has the effect of *reducing* the pairwise J_{ij} [8], and is the origin of the factor-of-three variations in

the NN J in Fig. 1.

We also considered the *ordered* limit, by putting 1 Mn in a 24-atom unit cell, corresponding to x=0.083. In this case P_1 decreases to 2/3, and T_c increases to 350K (see Fig. 3). Thus we conclude that ordering *increases* T_c, while clustering *decreases* T_c. Perhaps not suprisingly, the MFA T_c approaches the CVM result in the ordered case, since percolation is less critical.

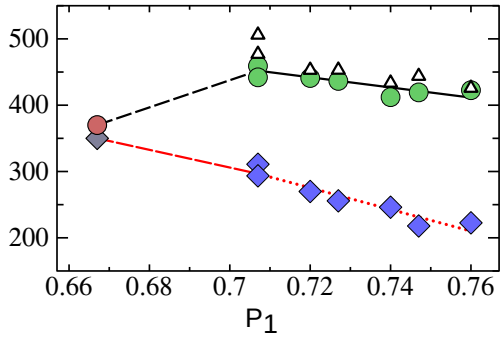

FIG. 3: Dependence of T_c (K) on the pair correlation function P_1 in $Ga_{0.92}Mn_{0.08}As$. The random (SQS) configuration corresponds to P_1=0.7056. (Two SQS structures were calculated.) Diamonds show T_c computed with CVM; circles show $\overline{T}_c^{MFA}$, and triangles show T_c^{MFA}. The point at $P_1 = 2/3$ corresponds to the ordered compound.

To conclude, we have shown that ferromagnetism is very sensitive to configurational disorder in DMS alloys, and that with proper treatment of disorder T_c is reasonably predicted by the LSDA for $Ga_{1-x}Mn_xAs$, without needing to invoke compensating defects. We briefly consider two important sources of error from elements missing in the theory. First, spin-orbit coupling strongly reduces T_c in $k\cdot p$ models. We estimated its effect by computing the change in $\overline{T}_c^{MFA}$ when the $L \cdot S$ coupling is added to the LSDA hamiltonion. For $Ga_{0.92}Mn_{0.08}As$, $\overline{T}_c^{MFA}$ was reduced by $\sim$10%. Finally, the LSDA itself will overestimate T_c somewhat [22]. In a future work we will present a reliable parameter-free theory that corrects the principal errors in LSDA—most importantly the Mn d character at E_F—and quantify the extent to which the LSDA overestimates T_c. Finally, we conclude that the present calculations represent a rather strict upper bound to T_c, and that for random or clustered $Ga_{1-x}Mn_xAs$ alloys, $T_c > 250$ K is unlikely.

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degrees of freedom which leads to a more complicated form for the partition function: $Z_{ij} = \sum_l (2l+1) i_l(\psi_i^{ij}/T) i_l(J_{ij}/T) i_l(\psi_j^{ij}/T)$, where $i_l(z) = \sqrt{(\pi/2z)} I_{l+1/2}(z)$ and $I_n(z)$ is the modified Bessel function of the first kind. Cluster methods can include strong correlation among atoms, which the MFA neglects. The CVM accurately describes interactions within the clusters (pair clusters in our case). The interactions of the cluster with the environment is described by renormalizing fields ψ^{ij}.

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